

# Supporting Information:

## Coordination and thermodynamic properties of aqueous protactinium(V) by first-principle calculations

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## Preparatory study on molecular geometries

Not many theoretical studies have been dedicated to protactinium(V) complexes. Therefore, we have performed a preparatory study on molecular geometries, with special emphasis on the  $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$  complex, for which both an EXAFS structure and a previously optimized B3LYP one were reported.<sup>S1</sup> We focus on key bond distances. In particular, we have tested:

1. Three electronic structure methods: MP2,<sup>S2</sup> DFT/B3LYP<sup>S3</sup> and DFT/PBE0;<sup>S4,S5</sup>
2. Two schemes for introducing the scalar relativistic effects, that is via the use of the all-electron Douglas-Kroll-Hess Hamiltonian<sup>S6-S8</sup> or via the use of a scalar relativistic energy-consistent pseudopotential, namely ECP60MWB;<sup>S9</sup>
3. Three basis sets, one all-electron one (SARC-DKH2<sup>S10</sup> for Pa and def2-TZVP<sup>S11</sup> for the other atoms) and two that are compatible with the ECP60MWB pseudopotential (with a segmented basis set<sup>S9</sup> for Pa and the def2-TZVP<sup>S11</sup> or aug-cc-VTZ<sup>S12</sup> ones for the other atoms);
4. Three different quantum chemistry codes, namely Gaussian,<sup>S13</sup> ORCA 4.2.1<sup>S14</sup> and OpenMolcas.<sup>S15</sup>

Not all the combinations have been tested, since a more limited number of cases was sufficient to reach the key conclusions that we needed to further proceed with the computations of ligand-exchange reaction constants. Results are presented in Tables S1 and S2.

The main objective of Table S1 was to compare results of all-electron calculations (columns 4 and 5) and of pseudopotential-based ones (columns 2 and 3). Three codes were used to perform these tests, because specific implementations that are not available in all the codes were required. We were first puzzled by the ORCA/B3LYP all-electron result, largely differing from the Gaussian/B3LYP one for which a pseudopotential was used. We have thus performed additional calculations with OpenMOLCAS. First, we have repeated the Gaussian/B3LYP calculation with the same generic setup (ECP60MWB/def2-TZVP), obtaining

Table S1: Comparison of codes and of all-electron *vs.* pseudopotential-based calculations for determining the structure of the  $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$  complex in the gas phase (all the distances are in Å).

	Gauss./B3LYP ECP60MWB def2-TZVP	OpenM./B3LYP ECP60MWB def2-TZVP	ORCA/B3LYP SARC-DKH2 def2-TZVP	OpenM./B3LYP SARC-DKH2 def2-TZVP
Pa–O <sub>oxo</sub>	1.862	1.862	1.792	1.871
av. Pa–O <sub>ligand</sub>	2.386	2.386	2.354	2.390
av. Pa–C	3.291	3.291	3.253	3.295
av. Pa–O <sub>ligand</sub> '	4.477	4.447	4.440	4.481

the exact same result. Thus, both the Gaussian and OpenMOLCAS implementations for pseudopotential calculations agree.

Then, we have repeated the all-electron SARC-DKH2/def2-TZVP calculations, finding a very different outcome than what was found with ORCA. After noticing the close matching between the all-electron OpenMOLCAS result and both the pseudopotential-based ones, we have looked for potential sources of errors in the ORCA/B3LYP calculation. It appeared that an extra simplification, in particular a one-center approximation, was present in the ORCA implementation for geometry optimization with the DKH2 Hamiltonian. Consequently, the ORCA/B3LYP result can be discarded and we conclude that the molecular geometries can be safely computed with both the ECP60MWB pseudopotential or with all-electron basis sets. For the sake of efficiency, we have thus chosen to follow the pseudopotential approach.

Table S2: Comparison of the B3LYP, PBE0 and MP2 optimized structures of the  $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$  complex in the gas phase (all distances in Å). All the calculations have been performed with Gaussian and made use of the ECP60MWB pseudopotential.

	EXAFS <sup>S1</sup>	B3LYP <sup>S1</sup> 6-31+G*	B3LYP def2-TZVP	PBE0	MP2	B3LYP aug-cc-pVTZ	PBE0	MP2
Pa–O <sub>oxo</sub>	1.75	1.89	1.862	1.843	1.855	1.863	1.845	1.862
av. Pa–O <sub>ligand</sub>	2.38	2.39	2.386	2.364	2.353	2.387	2.365	2.347
av. Pa–C	3.28	3.30	3.291	3.265	3.247	3.293	3.267	3.244
av. Pa–O <sub>ligand</sub> '	4.47	4.50	4.477	4.447	4.439	4.480	4.451	4.435

In Table S2, we have reported the previous EXAFS and B3LYP results,<sup>S1</sup> together with

new calculations with more advanced basis sets, namely the def2-TZVP and aug-cc-pVTZ ones. A few points deserve to be commented:

1. When all the B3LYP results are compared, two main behaviours are found: with the 6-31+G\* basis set, all the bond distances of interest seem overestimated, while a more consistent behaviour is observed with both the def2-TZVP and aug-cc-pVTZ basis sets, which are thus recommended;
2. For the three tested methods, the results obtained with either the def2-TZVP or aug-cc-pVTZ basis set are of equal quality; the def2-TZVP basis set, which is smaller, is thus preferable for efficiency purposes;
3. The MP2, DFT/PBE0 and DFT/B3LYP bond distances are very similar, all in good accord with the EXAFS structure, despite a remaining discrepancy on the Pa–O<sub>oxo</sub> bond;
4. The DFT/PBE0 method gives the Pa–O<sub>oxo</sub> bond distance in the closest agreement with experiment.

All in all, we have chosen to use the DFT/PBE0 method, the small-core ECP60MWB pseudopotential for Pa, and the def2-TZVP basis set for all the light atoms.

## Supplemental figure

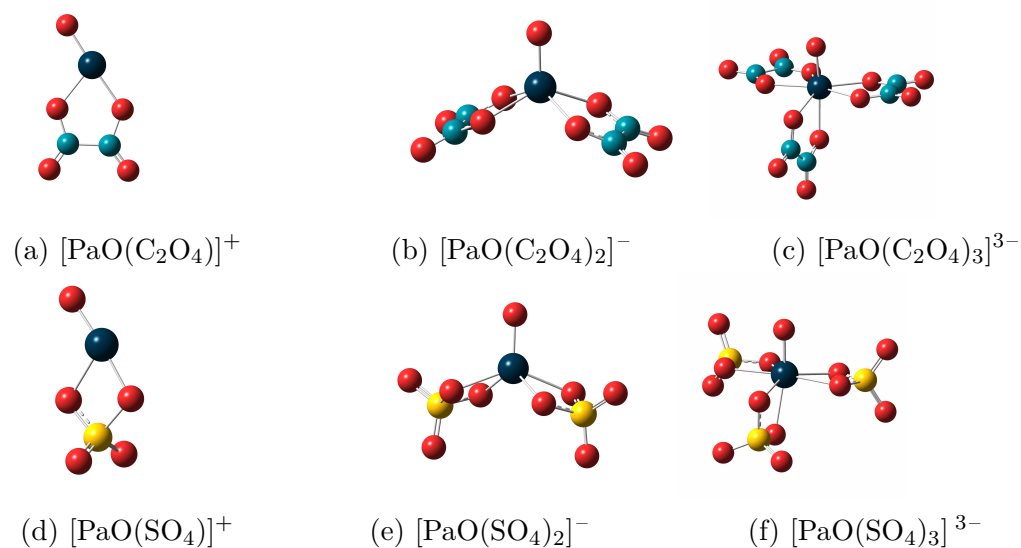


Figure S1: Representations of the GP(DFT/PBE0) structures of the Pa(V) complexes, obtained with unsaturated first-coordination spheres (corresponding to the structures of the bare complexes used in the “GP” and “PCM” columns of Table 2). Color code: dark blue (Pa), yellow (S), red (O) and light blue (C).

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